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Solar photo-Fenton for water disinfection: An investigation of the competitive role of model organic matter for oxidative species

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ABSTRACT

The competitive effect for the oxidative species produced during solar photo-Fenton process at neutral pH between an organic compound (resorcinol) and a model microorganism (*Enterococcus faecalis*) was investigated. With this purpose, the inactivation of *E. faecalis* was evaluated under several solar processes, i.e. SODIS, solar-UVA with H_2O_2 (10, 20 and 50 mg L^{-1}) and solar-UVA-Fe^{2+} (2.5, 5 and 20 mg L^{-1}) in the absence and presence of resorcinol (10 mg L^{-1}). The effect of resorcinol on the Fenton reaction (H_2O_2/Fe^{2+} in the dark: 5/2.5 and 50/20 mg L^{-1}) efficacy at neutral pH was also evaluated. In spite of resorcinol maintained a high amount of iron (around 10 mg L^{-1}) in solution during the experiments, with the highest concentrations of H_2O_2/Fe^{2+} (50/20 mg L^{-1}), only a 2-log decrease of bacteria was observed with 10 mg L^{-1} of resorcinol, while a 3.5-log abatement was detected without resorcinol. These results highlight the competitive role of organic matter for the oxidant species against bacteria when photo-oxidation and photo-disinfection processes are occurring at the same time. This competition for the oxidant species, mainly hydroxyl radicals generated during photo-Fenton, was confirmed by (i) the solar photo-Fenton assays at three different concentrations (H_2O_2/Fe^{2+}): 5/2.5, 10/5 and 20/10 mg L^{-1}, although at elevated concentrations of H_2O_2 and Fe^{2+} (50/20 mg L^{-1}) the disinfection efficiency was independent of the addition of resorcinol because an excess of radicals were generated, and (ii) by the photo-Fenton results obtained when the concentration of resorcinol was increased from 20, 30 till 40 mg L^{-1}.

1. Introduction

Water scarcity and groundwater contamination are serious problems since they affect to the human health. For these reasons, it is necessary to utilize treatments to ensure the water disinfection and reuse [1]. During wastewater treatment, the microbiological assessment of the water quality is usually carried out through the measurement of indicator microorganisms' concentration. *Escherichia coli* is the most commonly indicator of faecal contamination studied in wastewater disinfection. Parallel to the work on coliforms, a group of Gram-positive coccid bacteria known as faecal streptococci (FS) were being investigated as important pollution indicator bacteria [2]. Of the faecal streptococci, the preferred indicators of faecal pollution are the enterococci. The predominant intestinal enterococci are *Enterococcus faecalis*. Four key points in favour of the faecal streptococci were: (1) relatively high numbers in the excreta of humans and other warmblooded animals; (2) presence in wastewaters and polluted waters; (3) absence from pure waters, virgin soils and environments having no contact with human and animal life; (4) persistence without multiplication in the environment. Thus, according to the WHO guidelines on water quality, standards and health (2001), for water examination purposes enterococci, and particularly *E. faecalis*, can be regarded as indicators of faecal pollution of the water. Even, some authors have recently investigated on *E. faecalis* inactivation extrapolating their results for this model microorganism to bacterial consortia from wastewater treatment plant [3–5].

Recent studies propose the use of advanced oxidation processes (AOP) as alternative water disinfection technique. In particular, photo-Fenton may be used to efficiently treat wastewater contaminated with chemical pollutants [6,7] or pathogen microorganisms as bacteria, fungi, virus, etc. [8,9]. During the Fenton reaction, the hydrogen peroxide rapidly reacts with iron, and generates

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hydroxyl radicals, which are non-selective and highly oxidative species [10]. Iron is added at the beginning of the process and acts as a catalyst, being oxidized (Eq. (1)) and reduced continuously. Moreover, the presence of photons with wavelengths below around 550 nm (photo-Fenton system) leads to the generation of more hydroxyl radicals and regenerate Fe^{2+} (Eq. (2)) [10],

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^\bullet \quad (1)$$

$$[Fe(H_2O)]^{3+} + h\nu \rightarrow Fe^{2+} + HO^\bullet + HO^+ \quad (2)$$

The optimal pH of this process is 2.8, being much less efficient at near neutral pH due to the low solubility of iron salts at this pH. Hence, some authors are carrying out new research to overcome this problem. Some researchers have used specific systems to immobilize the iron. Cho et al. [11] employed a photo-ferrioxalate disinfection system (UV–visible light ions and oxalate), which allowed to obtain dissolved Fe^{3+} necessary for *E. coli* inactivation at neutral pH. Also, a woven inorganic silica fabric with Fe ions into (EGF-Fe) was checked in the inactivation of *E. coli K12* by photo-Fenton [12]. One of the most studied options consists of using different iron complexing as ethylenediamine-N,N′-disuccinic acid (EDDS) [13]. Klamerth et al. [13] showed that iron complexation with EDDS leads to stabilization and solubilization of Fe at natural pH although bacteria disinfection was not complete. Spluher et al. [14] reported that resorcinol, as a model of natural organic matter (NOM) present in the wastewater, improved the solubility of iron during the photo-Fenton process. Resorcinol and its degradation intermediates formed complexes with iron which were photoactive at neutral pH. The generation of reactive oxygen species was favoured leading to inactivation times for *E. coli* lower than when resorcinol was not present in the water [14].

However, the main challenge to disinfect wastewater containing organic matter is to achieve both chemical detoxification and microbial inactivation at the same time during the photocatalytic treatment. The presence of organic substances naturally present in water like dihydroxybenzenes isomers (resorcinol among others) showed a negative effect on photocatalytic disinfection of *E. coli* with TiO_2 [15]. Cho et al. [11] performed the inactivation of *E. coli* by TiO_2 in the presence of methanol as hydroxyl radical scavenger. Their results showed that methanol significantly inhibited *E. coli* inactivation (inactivation lower than 0.5-log in 60 min). Marugán et al. [16] studied the TiO_2 photocatalytic treatment for methylene blue chemical oxidation and *E. coli* inactivation. They concluded that changes in the activity for the oxidation of the organic molecule cannot be extrapolated to the photocatalytic disinfection processes. However, observations of Chen et al. [17] indicated that there was an apparent correlation between the two photocatalytic processes of decomposing formaldehyde and inactivating *E. coli* for TiO_2 treatment.

The aim of this research was to study the role of an organic molecule as resorcinol (considered as a model of NOM) on the disinfection process by solar photo-Fenton at neutral pH; so that the accelerating or competitive effect of this organic matter was discriminated. A deep study on the variables involved, i.e. reagents dosage and concentration of organic compound was performed. With this purpose, inactivation of *E. faecalis* was investigated by solar disinfection (SODIS), UVA-H_2O_2, UVA-Fe^{2+} and Fenton reaction. *E. faecalis* disinfection by solar photo-Fenton was evaluated with four initial concentrations of H_2O_2 and Fe^{2+}. The concentration of resorcinol in all assays was 10 mg L^{-1}. Finally, the *E. faecalis* inactivation by photo-Fenton was also evaluated with higher concentrations of resorcinol. Experiments without resorcinol were included in all experiments as reference.

2. Materials and methods

2.1. Bacterial strain and inoculum preparation

E. faecalis CECT 5143 was acquired from the Spanish Culture Type Collection (Colección Española de Cultivos Tipo, Valencia, Spain). Cultures of *E. faecalis* were grown in Streptococcus Selective Broth media (Biolife) and incubated at 37 °C with constant agitation in an orbital shaker at 150 rpm for 24 h. *E. faecalis* was harvested in stationary phase by centrifugation at 3000 rpm for 10 min and washed three times with saline solution (0.9% NaCl) obtaining a final bacterial concentration of 10^6 CFU mL^{-1} (determined by optical density at 600 nm). The required stock volume was added to saline solution in order to avoid osmotic stress and its resultant detrimental effect on cell viability during the experiments. Saline solution was prepared with sterile Milli-Q water.

2.2. Experimental procedure

Inactivation of *E. faecalis* was investigated using the following solar promoted processes: (i) solar disinfection ($SODIS_{[0]}$); (ii) solar UVA with added H_2O_2 at 10, 20 and 50 mg L^{-1}; (iii) solar UVA-Fe^{2+} (2.5, 5 and 20 mg L^{-1}); and (iv) Fenton reaction at two concentrations of reagents H_2O_2/Fe^{2+}: 5/2.5 and 50/20 mg L^{-1}; (v) *E. faecalis* disinfection by solar photo-Fenton was evaluated at four different concentrations of hydrogen peroxide and iron (H_2O_2/Fe^{2+}): 5/2.5, 10/5, 20/10 and 50/20 mg L^{-1}. Resorcinol was present at same concentration, 10 mg L^{-1}. Finally, other photo-Fenton tests were also carried out at higher concentrations of 20, 30, and 40 mg L^{-1}. As a reference, photo-Fenton experiments were also done without resorcinol. The experiments were done in triplicate, the results did not show significant statistical variations (the confidence level was greater than 95%).

All experiments were carried out in 250 mL Duran-Glass (Schott, Germany) stirred tank reactors under natural sunlight. Glass covers were used to allow the solar radiation to enter the reactor from all directions. The reactors were stirred at 150 rpm during the experiment. The UVA radiation and temperature was measured online during the experiments with a radiometer (Delta OHM LP UVA 02 model) and with a probe (Crison 60 50), respectively. Data were obtained by a data acquisition card (LabJack U12) connected to a computer. Mean temperature and UVA radiation values were 28 ± 1 °C and 30 ± 2 W m^{-2}, respectively.

For all experiments, prior to bacterial spiking, a control sample was taken to check the non-presence of any other microorganisms in the Milli-Q water. Bacterial suspension was mixed for 2 min in the dark and a second control sample was taken. This control was kept in the lab (in the dark, at room temperature) and plated at the start and end of the experiment to check cell viability without undergoing any of the treatments. The samples taken during the experiments were enumerated using the standard plate counting method through 10-fold serial dilutions in Streptococcus Selective Broth (Biolife, Italy) (30.6 g L^{-1}) and agar (15 g L^{-1}). A volume of 20 μL was plated three times for each one of the four 1:10 dilution. Colonies were counted after 24 h incubation at 37 °C. The detection limit was 1 CFU mL^{-1}. This procedure was carried out in triplicate for each sample. In order to test cell recovery post-treatment, the samples were maintained in the dark after the treatment for predetermined exposure times. These samples were plated for colony counting after a 24 h period.

2.3. Analytical determinations

Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$ >99%, Fluka, Spain) was used as a source of Fe^{2+}. Iron concentration was analyzed by the o-phenantroline standardized method according to ISO 6332.

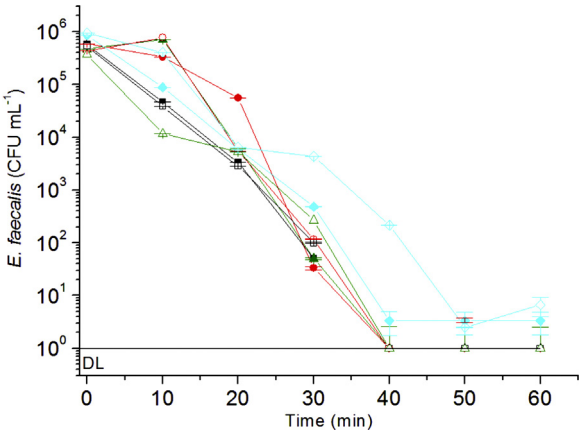

Fig. 1. Effect of resorcinol on *E. faecalis* inactivation by solar UVA – H_2O_2 as a function of H_2O_2 concentration (mg L^{-1}): SODIS (-◆-); 10 (-●-); 20 (-■-) and 50 (-▲-). Closed symbols: 10 mg L^{-1} resorcinol. Open symbols: no resorcinol added. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

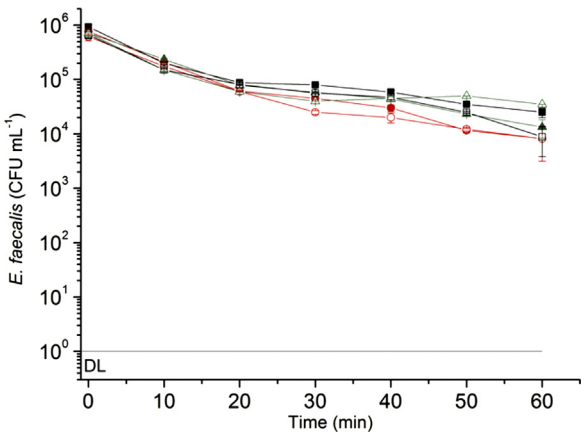

Fig. 2. *E. faecalis* inactivation by solar – Fe^{2+} with 2.5 (-●-), 5 (-■-) and 20 (-▲-) mg L^{-1} of Fe^{2+}. Closed symbols: 10 mg L^{-1} resorcinol. Open symbols: no resorcinol added. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Hydrogen peroxide (30%, w/v aqueous solution, Sigma–Aldrich, Spain) concentration was measured with the ammonium metavanadate method. Any hydrogen peroxide present in the samples was removed using catalase (Fluka, Spain) to avoid hydrogen peroxide in the dark after sampling. Resorcinol ($C_6H_6(OH)_2$) was acquired from Fluka. It is a white solid crystalline substance with a molecular weight of 110.11 g mol^{-1} and its solubility in water is 0.123 g L^{-1}. Its concentration was measured via UPLC (Agilent Technologies, series 1200). A reverse-phase column (Agilent XDB-C18) was used as the stationary phase. The mobile phase consisted of a mixture of 5% analytical-grade acetonitrile and 95% ultrapure water (Millipore Co.). All water samples were filtered with 0.2 μm syringe-driven filters (Millex®, Millipore).

3. Results and discussion

3.1. Individual effects of solar light, hydrogen peroxide and iron concentrations on E. faecalis inactivation with and without resorcinol

Prior to study the effect of resorcinol on photo-Fenton process for *E. faecalis* inactivation, several experiments were carried out in order to determine if there was any resorcinol photo-degradation under sunlight or by the interaction with hydrogen peroxide. These experiments were: resorcinol (10 mg L^{-1}) under sunlight (solar-resorcinol), resorcinol with different concentrations of Fe^{2+} (2.5, 5, 10 and 20 mg L^{-1}), and resorcinol with three concentrations of H_2O_2 (10, 20 and 50 mg L^{-1}) in the absence of bacteria. During these tests resorcinol concentration was monitored by UPLC along the experiment, and in any of them, resorcinol was not degraded (data not shown).

Subsequently, the effects of individual processes involved in the photo-Fenton treatment of *E. faecalis* were previously determined. Therefore, solar light, H_2O_2/solar, Fe^{2+}/solar and Fenton (H_2O_2/Fe^{2+}) experiments were carried out for *E. faecalis* inactivation with 10 mg L^{-1} of resorcinol and without resorcinol. As expected, the mere action of sunlight over *E. faecalis* cells (SODIS) had high disinfecting performance although the detection limit was not achieved in any case (Fig. 1). The addition of H_2O_2 (10, 20 and 50 mg L^{-1}) improved bacterial inactivation, so that the detection limit was reached in 40 min under full sunshine exposure (Fig. 1). The bacterial damage was independent of the hydrogen peroxide concentration as the lowest hydrogen peroxide concentration (10 mg L^{-1}) was lethal for the bacteria. Some research articles have reported on the killing effect of UVA-H_2O_2 over several microorganisms in water [18–21]. The inactivation is induced by several damages such as the DNA damage due to the reactive oxygen species ROS ($O_2^{\bullet}$, $HO^{\bullet}$, H_2O_2) produced by sunlight [22] and the Haber–Weiss reaction occurring when the H_2O_2 intra molecular levels increase and react with the internal 'free iron' generating hydroxyl radicals and lethal effects inside cells [14].

During these tests, the H_2O_2 concentration was monitored and not significant consumption was detected when resorcinol was not present. The decrease in hydrogen peroxide concentration due to its diffusion inside the cells is negligible compared to the added hydrogen peroxide. Therefore, there is no correlation between the H_2O_2 decrease and the disinfecting effect, as other contributions in this field stated [23]. Equally, when resorcinol was added, no significant consumption of hydrogen peroxide was detected; which is in concordance with the constant concentration of resorcinol measured during the experiment.

E. faecalis inactivation during solar-Fe^{2+} (2.5, 5 and 20 mg L^{-1}) process in absence or presence of 10 mg L^{-1} of resorcinol was studied. The inactivation results were the same for all concentrations of Fe^{2+} tested, with a decrease between 1.5 and 2-log in the bacterial concentration with and without resorcinol (Fig. 2). As other authors suggest [14] the inactivation can be explained because Fe^{2+} can react with O_2 leading to the formation of ROS, which promote the attack to the membrane enhancing its permeability and roughness. Also, Fe^{2+} diffuses into the cells and catalyses the reduction of metabolic hydrogen peroxide leading to the generation of hydroxyl radical via intracellular Fenton [24]. However the disinfection process is clearly disfavoured in presence of Fe respect to the SODIS experiment due to the light screening effect of the iron solution.

3.2. Effect of Fenton reaction on E. faecalis with and without resorcinol

E. faecalis inactivation by Fenton at neutral pH was evaluated in presence and absence of resorcinol. To this end, two extreme conditions of Fenton were used. The first case, at low reagent concentrations (2.5 mg L^{-1} of Fe^{2+} and 5 mg L^{-1} of H_2O_2), and the second one at high concentrations (20 mg L^{-1} of Fe^{2+} and 50 mg L^{-1} of H_2O_2). When the lowest reagents concentration was used, the bacterial concentration remained constant at 10^6 CFU mL^{-1} during the experiment regardless the added resorcinol (Fig. 3a), probably due to the experimental conditions were not enough oxidant. At this mild condition, resorcinol is not totally degraded (Table 1).

Table 1
Hydrogen peroxide and resorcinol concentrations during Fenton reaction at two concentrations of reagent assayed: H_2O_2 = 5, 50 mg L^{-1} and Fe^{2+} = 2.5, 20 mg L^{-1} with resorcinol (10 mg L^{-1}) and without resorcinol.

Time (min)	H_2O_2 = 5 mg L^{-1} and Fe^{2+} = 2.5 mg L^{-1}			H_2O_2 = 50 mg L^{-1} and Fe^{2+} = 20 mg L^{-1}		
	Without resorcinol	With resorcinol		Without resorcinol	With resorcinol	
	H_2O_2 (mg L^{-1})	H_2O_2 (mg L^{-1})	Resorcinol (mg L^{-1})	H_2O_2 (mg L^{-1})	H_2O_2 (mg L^{-1})	Resorcinol (mg L^{-1})
0	5	5	10	50	50	10
10	5.1	1.7	3.4	33.5	25.2	4.2
20	4.5	0	2.4	31.9	22.9	0
30	4.4	0	2.1	30.8	21.5	0
40	4.3	0	2.0	30.4	20.6	0
50	0	0	2.0	30.3	20.4	0
60	0	0	2.0	29.2	18.2	0

For the highest reagents concentrations, the inactivation of *E. faecalis* was of 2-log (with resorcinol) and 3.5-log (without resorcinol), and resorcinol degradation was complete within 20 min of reaction (Table 1). These results highlight the competition between degradation and disinfection process; which is in concordance with previous investigations [11,15–17]. In these works, organic substances like dihydroxybenzenes isomers (resorcinol among others) [15], MeOH [11] and methylene blue [16] showed a negative effect on the disinfection of water with *E. coli* by TiO_2 photocatalytic treatment.

In presence of resorcinol, HO• attacks this organic molecule leading to a decrease of oxidative attack to bacterial cells. Therefore, when resorcinol is not present in solution, more hydroxyl radicals are available to attack *E. faecalis* cells. These results are supported by the hydrogen peroxide consumption during Fenton reaction. In both experiments, with 10 mg L^{-1} of resorcinol, the H_2O_2 consumption was faster because the dissolved iron was higher (Table 1, Fig. 3b).

During Fenton treatment, resorcinol was partially or totally degraded (depending of oxidative conditions of the Fenton reaction) by hydroxyl radicals (Table 1); where the dissolved iron was maintained at different values (Fig. 3b). When the added iron salt was 20 mg L^{-1}, we observed that 10 mg L^{-1} of Fe^{2+} was dissolved through the experimental time (1 h) in the presence of resorcinol, and decreased until 2 mg L^{-1} in the absence of resorcinol. For the case of added 2.5 mg L^{-1} of Fe^{2+}, resorcinol helped to keep this concentration in solution, while in its absence the dissolved iron decreased until nearly zero (Fig. 3b). Spluher et al. [14]

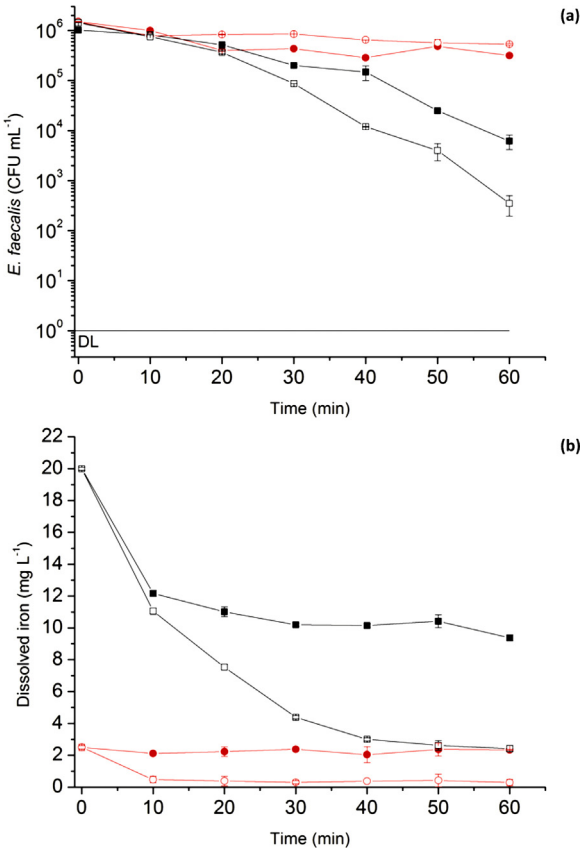

Fig. 3. (a) *E. faecalis* inactivation by Fenton reaction with two levels of H_2O_2/Fe^{2+} concentrations (mg L^{-1}): 5/2.5 (-●-) and 50/20 (-■-). (b) Concentration of dissolved iron. Closed symbols: with 10 mg L^{-1} of resorcinol. Open symbols: no resorcinol. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

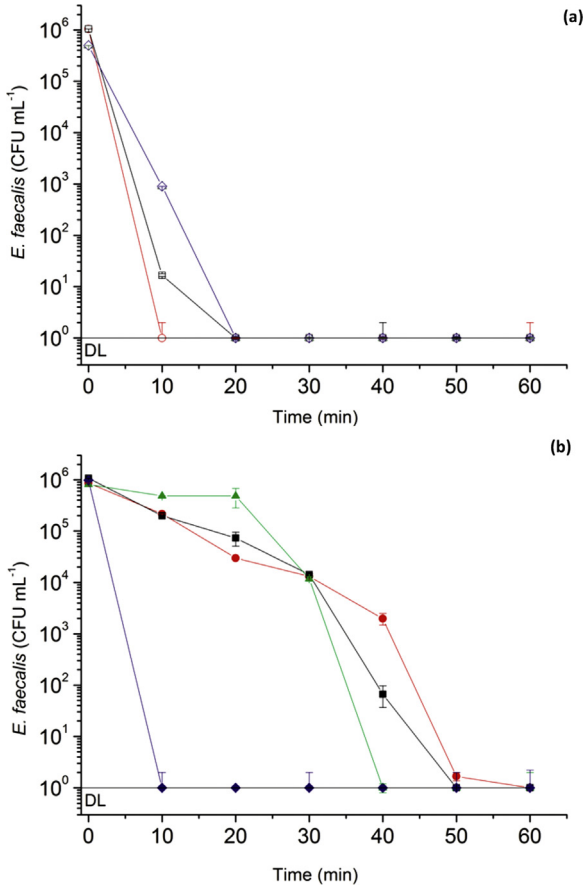

Fig. 4. *E. faecalis* inactivation by photo-Fenton (a) H_2O_2/Fe^{2+}: 5/2.5 (-○-), 10/5 (-□-), 20/10 (-△-) and 50/20 (-◇-) mg L^{-1} without resorcinol and (b) H_2O_2/Fe^{2+}: 5/2.5 (-●-), 10/5 (-■-), 20/10 (-▲-) and 50/20 (-◆-) mg L^{-1} with resorcinol (10 mg L^{-1}). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

established that intermediates generated during resorcinol mineralization form Fe^{3+}-organo bounds which are stable at near neutral pH leading to a higher iron-photo-assisted *E. coli* inactivation in presence of resorcinol. The differences with the observations in this research could be attributed to the high reagent concentrations used, which provide sufficient dissolved iron although resorcinol was not added (Fig. 3b). Moreover, *E. coli* (Gram-negative bacteria) is more sensitive to the treatment than *E. faecalis* (Gram-positive bacteria) [23]. The peptidoglycan layer in *E. faecalis* is thicker than that of *E. coli* and therefore much more difficult to destroy. In wastewater containing sensitive bacteria as *E. coli* a low concentration of $HO^{\bullet}$ is enough to achieve an adequate disinfection which is favoured if iron is in solution. However, if more resistant bacteria are present, the presence of organic compounds that are easily attacked by hydroxyl radicals (as resorcinol or other aromatic substances) disfavour the disinfection process. Therefore, it is very important to investigate microorganisms that are more resistant to disinfection processes than *E. coli*, which is too sensitive as compared with other bacteria and therefore it is not a good model for disinfection studies [8].

3.3. *E. faecalis* inactivation by solar photo-Fenton: effect of resorcinol

E. faecalis disinfection by solar photo-Fenton at neutral pH was evaluated with ($10\,mg\,L^{-1}$) and without resorcinol in four assays at different initial ratios between hydrogen peroxide and iron (H_2O_2/Fe^{2+}): 5/2.5, 10/5, 20/10 and 50/20 $mg\,L^{-1}$. As Fig. 4a shows, there were no marked differences in the disinfection efficiency when resorcinol was not present in the water regardless the concentration of reagents. Iron and hydrogen peroxide have an important influence on the generation of hydroxyl radicals, so that an increase in the initial concentration would result in more radical production [25]. In the most oxidative condition (H_2O_2/Fe^{2+}: $50/20\,mg\,L^{-1}$) a more efficient disinfection result would be expected. Nevertheless, at a view of the results, it seems that the lowest oxidative conditions (H_2O_2/Fe^{2+}: $5/2.5\,mg\,L^{-1}$) produce enough lethal damage to achieve complete disinfection in less than 10 min of reaction time.

On the contrary, when resorcinol is present, a marked delay in the disinfection process compared with the same process without resorcinol was observed (Fig. 4b). Therefore, these results confirm the competition between degradation and disinfection processes during Fenton treatment. Moreover, in presence of resorcinol (Fig. 4b), as H_2O_2/Fe^{2+} concentrations increase from 5/2.5 to 50/20 $mg\,L^{-1}$ *E. faecalis* the inactivation also enhances. The concentration of resorcinol is the same in these experiments; and the photo-Fenton reagents concentration increase, leading to a higher hydroxyl radical amount generation. Therefore, more radicals are available to attack the bacteria and consequently the inactivation is enhanced. This hypothesis is supported by the results at H_2O_2/Fe^{2+}: $20/50\,mg\,L^{-1}$, where the disinfection is independent of the addition of resorcinol. At this concentration, the formation of radicals is so high that the attack to the resorcinol ring does not result in a detrimental effect on the bacterial inactivation (Fig. 4a and b). Recently, competition between organic matter degradation and microbial inactivation during the photo-Fenton reaction has been demonstrated. Polo-Lopez et al. [21] observed a clear competition between organic matter and *Fusarium solani* spores for H_2O_2, hydroxyl radicals and other ROS, during photo-Fenton reaction. The

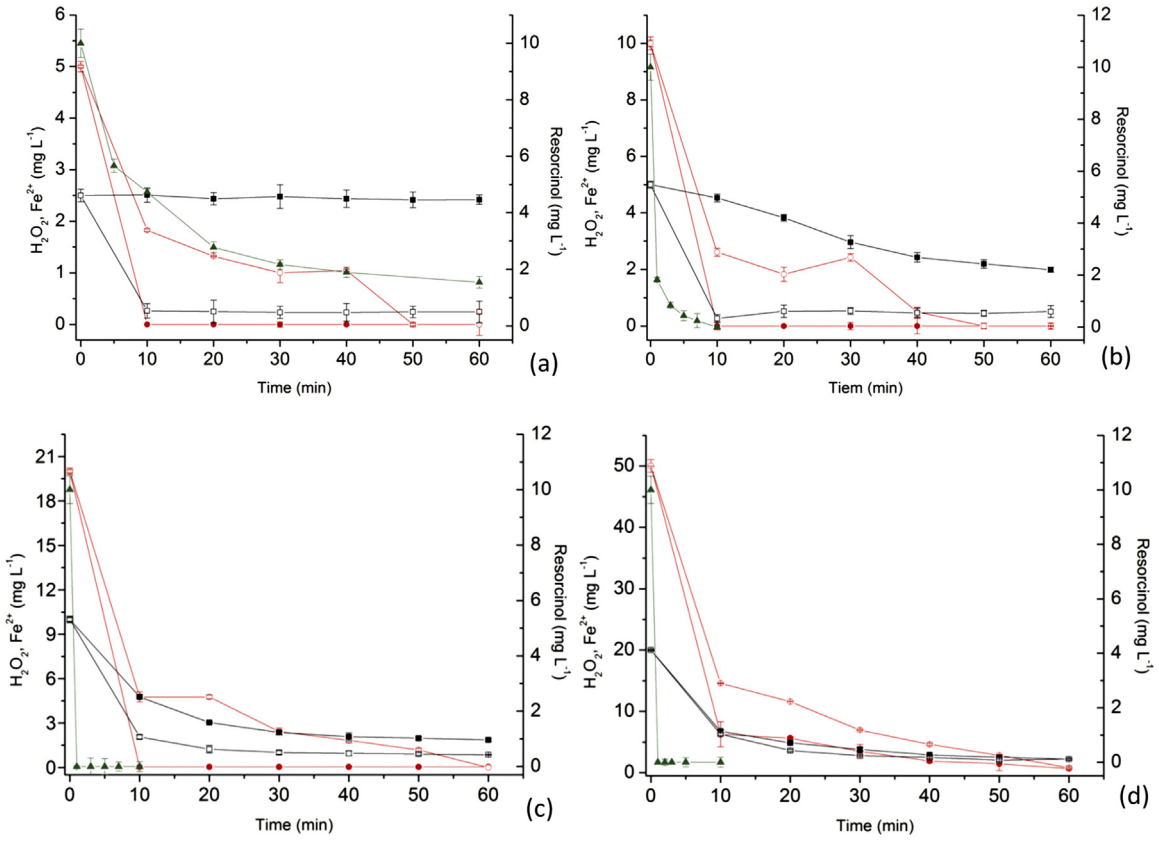

Fig. 5. H_2O_2 (–●–), Fe^{2+} (–■–) and resorcinol (–▲–) concentrations during disinfection of *E. faecalis* by photo-Fenton in presence of resorcinol ($10\,mg\,L^{-1}$) at different concentrations of H_2O_2/Fe^{2+}: (a) 5/2.5, (b) 10/5, (c) 20/10 and (d) 50/20 $mg\,L^{-1}$. Open symbols: no resorcinol added. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

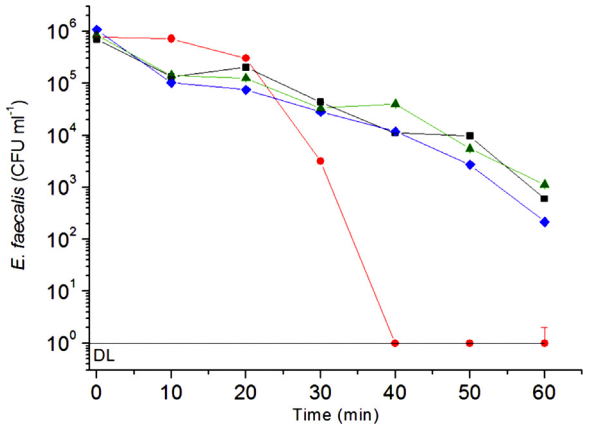

Fig. 6. *E. faecalis* inactivation by photo-Fenton (H_2O_2/Fe^{2+}: 10/5 mg L^{-1}) with 10 (-●-), 20 (-■-), 30 (-▲-) and 40 (-◆-) mg L^{-1} of resorcinol. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

inactivation of spores was disfavoured although the mineralization was enhanced.

The behaviour of hydrogen peroxide consumption is critical to explain the observed differences when resorcinol is present during the disinfection process. As in the Fenton process (Section 3.2), regardless the reagents concentration, H_2O_2 consumption was faster when resorcinol was added also in the photo-Fenton treatment (Fig. 5a–d). The same behaviour was observed in blank experiments (without bacteria, data not shown). In the four tested conditions, if resorcinol was added, the intermediates from resorcinol photo-degradation were able to maintain ~2.5 mg L^{-1} of Fe^{2+} in solution (Fig. 5). When resorcinol was not added, the concentration of iron was 0.2, 0.5, 0.8, and 2.2 mg L^{-1} at initial Fe^{2+} concentration of 2.5, 5, 10 and 20 mg L^{-1}, respectively. These low concentrations of iron still lead to a complete inactivation (until detection limit) of *E. faecalis* by photo-Fenton. Resorcinol was degraded in all cases in less than 5 min, except for the lowest reagents concentration, where an 80% of degradation was achieved at 60 min of treatment (Fig. 5). The same behaviour and degradation rate was observed for resorcinol in the blank photo-Fenton experiments (without bacteria, data not shown), which demonstrates the strong probability of attack of hydroxyl radicals formed during the solar photo-Fenton to the organic molecule.

In order to corroborate the competition between disinfection and chemical photo-oxidation processes, additional experiments were carried out increasing the added concentration of resorcinol (10, 20, 30 and 40 mg L^{-1}) using solar photo-Fenton with 5 of Fe^{2+} and 10 mg L^{-1} of H_2O_2. These tests were carried out simultaneously (Fig. 6). When the concentration of the resorcinol increases the inactivation was clearly disfavoured, although above 20 mg L^{-1} of resorcinol, no significant differences in the inactivation results were detected. This behaviour may be attributed to the consumption of the hydroxyl radicals generated during the photo-Fenton process with 20, 30 and 40 mg L^{-1} of resorcinol. A complete degradation of resorcinol was observed at 10 mg L^{-1}, while a 78, 45 and 40% of degradation was attained at 20, 30 and 40 mg L^{-1} of resorcinol, respectively.

4. Conclusions

An experimental study on the effect of resorcinol (a model of natural organic matter) over the efficiency of Fenton and photo-Fenton at near neutral pH for water disinfection polluted with *E. faecalis* has been carried out. The presence of resorcinol has been proven to help to maintain relatively high levels of the dissolved iron in the water at neutral pH. However, the addition of resorcinol decreases the disinfection efficiency as this compound competes for the hydroxyl radicals generated during both, Fenton and photo-Fenton processes. Therefore, the positive effect of adding resorcinol to maintain dissolved iron is blocked by the competitive role of the organic matter for the oxidant radicals. This competence between disinfection and photo-oxidation process was not observed when very oxidant conditions were applied during photo-Fenton process (H_2O_2/Fe^{2+}: 50/20 mg L^{-1}) because an excess of radicals were generated. *E. faecalis*, as indicator of water quality, has been shown to be a good model for disinfection research since it permits discerning the interaction between the bacteria and organic matter. This has important implications in the study of photo-Fenton for water purification, i.e. disinfection and decontamination.

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